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COLLOIDS COMPLICATE TREATMENT PROCESSES

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Colloids complicate treatment processes

High molecular weight polymers from biological treatment have a pronounced effect on separation processes

The colloidal matter which remains in effluents from biological treatment plants is derived from the microbial organisms that bring about the treatment. This biological treatment usually is called secondary treatment because many large plants precede it by primary settling and skimming. The microorganisms may be used in a homogeneous aerated reactor, as in the activated sludge process, or they may be attached to surfaces in a heterogeneous reactor called a trickling or biological filter. A trickling filter has large pores(2-5 cm.), and removes particulate matter by adsorption rather than by straining. Most experimental work has been done with activated sludge; however, the effluents from trickling filters are qualitatively similar.

The colloidal content of raw sewage has been measured; of particular interest is the early work of Gehm (1939), who defined soluble materials in sewage, "for practical purposes," as those passing a Seitz filter, thus distinguishing them from larger colloidal material. Gehm recognized that dispersed colloids may pass the filter but showed that they are a very small fraction of raw sewage. Unfortunately, later authors have used the terms filterable and soluble interchangeably. A Seitz bacteriological filter has pores which are about 0.2 micron in diameter. Modern definitions of "soluble" make use of a membrane filter, of the type to collect bacteria, which has 0.45 micron pores. This range approximates the 0.2-0.5 micron classical upper limit for dispersed colloids. Thus, the term "soluble matter" in waste water frequently included dispersed colloids. All authors agree that the colloidal material in raw sewage is increased by any form of biological attack.

Flocculants

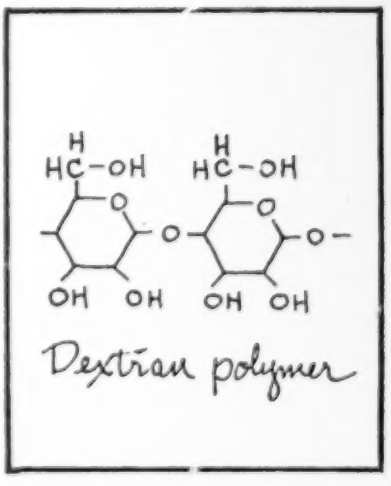
Polymeric organic flocculants and/or colloidal inorganic hydroxides of iron, aluminum, or silicon may be used to aid sedimentation in the primary unit. Residues of these flocculants and other suspended matter that escapes primary treatment are almost entirely removed in secondary treatment by adsorption to organic flocs or slimes. The normal concentration of suspended solids entering an activated sludge stage is of the order of 60 mg./l. This is mixed with about 2400 mg./l. of activated sludge solids consisting of living and dead bacteria, other microorganisms, and associated slimes. After aeration, the sludge flocculates and settles, leaving an effluent with less than 20 mg./l. of suspended solids. Only a small fraction of these suspended solids would be expected to have come through unchanged from the primary effluent. Suspended and colloidal matter in secondary effluents thus consists almost entirely of biological substances manufactured by the organisms and not completely removed in the final clarifier.

Bacteria

The suspended solids of a good secondary effluent consist largely of bacteria agglomerated in small flocs, and are not significantly different in composition from the return sludge. The associated colloidal matter has been fractionated, and electron micrographs of the colloidal fractions showed compact particles such as viruses and phages, flagella, and cellular debris. I have applied liquid nitrogen freeze-drying techniques developed in Sweden to secondary effluents that had been filtered to remove flocs. The dominant particulate matter found was fragments of bacterial cell walls. These have been described as bag-shaped macromolecules by other workers who showed that the fragments consist of a polymeric net with amino sugars running one way as a warp, tied together with a polypeptide woof. Virus and phages, flagella, and other cellular appendages represent a minor portion of the resolvable colloids.

Of greater importance is an appreciable quantity of non-resolvable colloids which are aggregated by freeze-drying. Among these substances are the type of hydrocolloids extracted from sludge by Busch and Stumm. These authors centrifuged activated sludge and precipitated an anthrone positive carbohydrate flocculant from the supernatant liquid by dilution with ethanol. The material extracted in this way was shown to be a negatively charged hydrocolloid that was an effective flocculating agent for silica particles and for pure cultures of dispersed bacteria.

Bacteria produce a great variety of polymeric substances that are exuded



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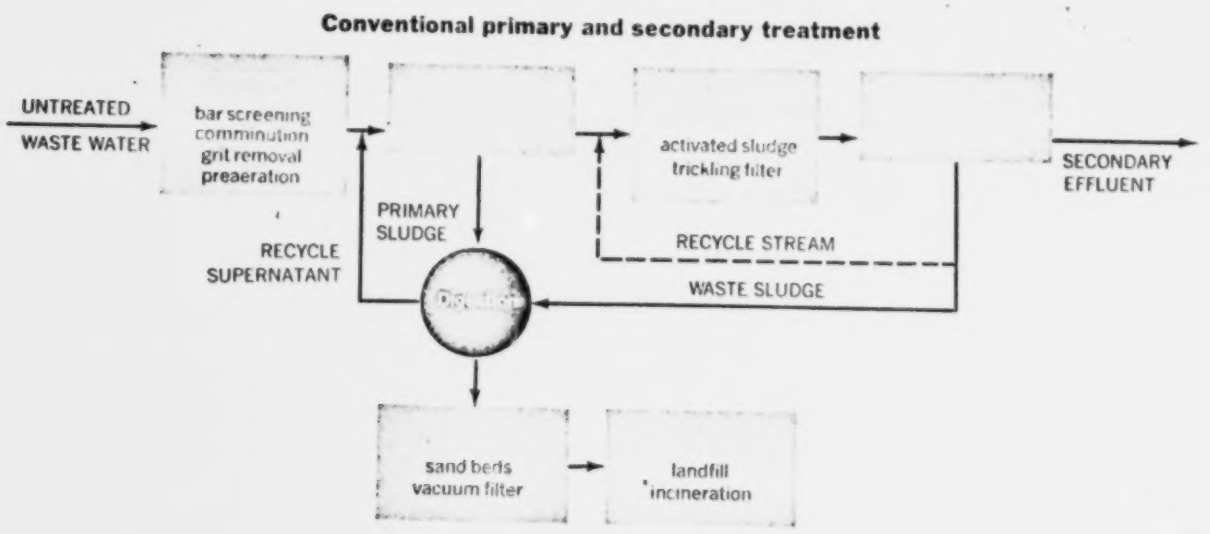


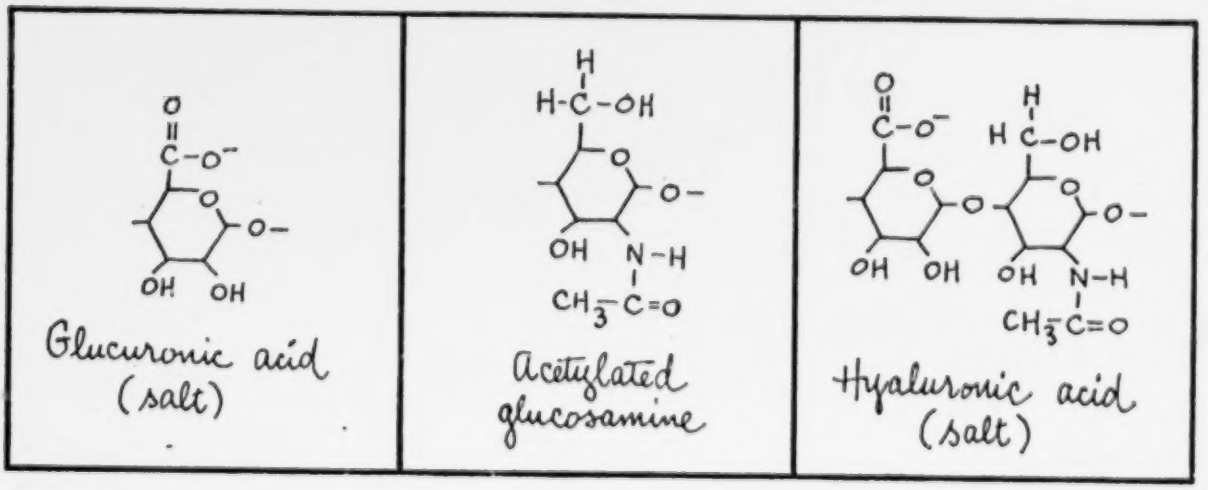
as a slime or that form a soft capsule which may occupy 10 or more times the volume of the cell. In addition, cells which die during treatment rupture or lyse and liberate their contents. Most of the contents of lysed cells are, however, taken up as food by other bacteria, in contrast to capsular material and cell walls which are inherently more resistant to metabolic degradation. A large number of hydrocolloids have been identified in capsular material and slimes. The chemically simplest is the polysaccharide dextran which has been harvested from bacterial cultures for use as a blood plasma extender. Dextran—an uncharged glucose polymer analogous to cellulose, starch, and glycogen—is a poor flocculant.

Polysaccharides

The most common group of slimes consists of the polysaccharide gums, which are similar to commercial plant gums such as gum arabic and alginates. Stacey and Ba'ker (1960) present lists of the simple carbohydrates which have been identified in the capsular material of *Salmonella* and *Aerobacter*. The most extensively studied group of bacterial slimes is that of the *Pneumococci*. The capsular material of these organisms gives highly specific immunological reactions which are the basis for differentiating strains. These type-specific polysaccharides have molecular weights of the order of one million. Salton (1960) lists the monosaccharides that constitute the capsular polysaccharides of 11 strains of *Pneumococci*. Each type has a distinctive monosaccharide composition. The simple sugars—glucose, rhamnose, and galactose—appear in combinations with uronic acids and amino sugars.

While *Pneumococci* are not found in large numbers in activated sludge, very similar polysaccharides have been found in other species that have been less thoroughly investigated. It is only to be expected that the mixed flora of biological treatment plants will produce complicated mixtures of polysaccharide gums and other slime forming substances.

Substantial quantities of nonprotein nitrogen are present in the amino sugars of bacterial cell walls and slimes. Since the amine group appears always as an acetyl derivative, it does not contribute a positive charge. The carboxylic groups of uronic acids over the pH range found in waste water will always be negatively ionized. Thus, the polysaccharides are negative hydrocolloids with a highly heterogeneous composition. A widely occurring polysaccharide, hyaluronic acid, composed of a glucuronic acid alternating with an acetylated glucosamine, appears to be identical to hyaluronic acids of mam-

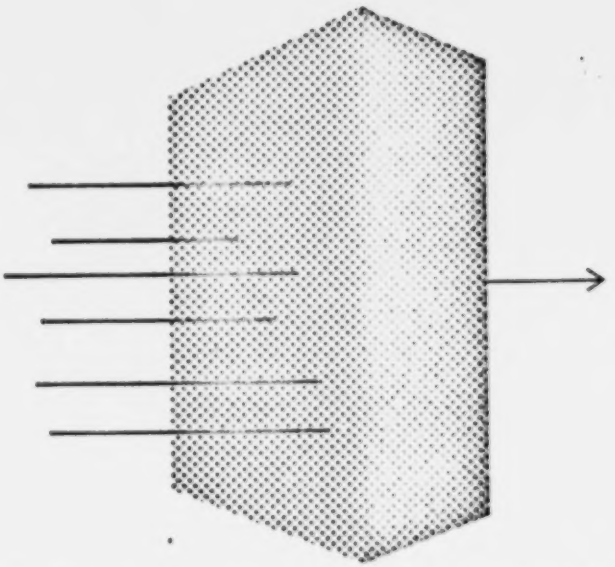


malian origin. Some bacteria produce hyaluronidase that hydrolyzes the capsular material of other organisms and exposes them to attack.

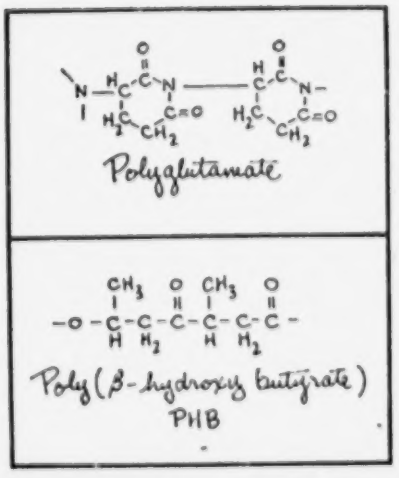
Another type of capsular material is composed of amino acids such as proteins and the polypeptides of glutamic acid. Both *d* and *l* isomers have been identified and both alpha and gamma carboxyl groups may take part in chain formation. Free carboxyl groups are absent in the intact capsule, suggesting the presence of intramolecular secondary amides.

Partial hydrolysis of material liberated from the capsules would liberate some free carboxyl groups and confer a negative charge on the polymer. Polyglutamic acid is a water soluble hydrocolloid with an isoelectric point near pH 4. Polyglutamates, although they are technically not proteins, would be included with proteins in a proximate analysis of the organic matter.

A third type of flocculating material is the linear polymre of beta-hydroxybutyric acid (PHB). This polymer is a chloroform soluble lipid that is insoluble in water and adheres to wetted surfaces. It is formed inside the bacterial cells, and has been implicated in the process of causing agglutination of the cells and other suspended solids. Up to 50% of the cell volume can be occupied by PHB, which is a reserve food that is stored like glycogen when food supplies are plentiful. Under some conditions, PHB is associated with floc formation in activated sludge. Since it is primarily an intracellular water insoluble polymer, PHB is not expected to represent a substantial fraction of the colloids in secondary effluent.



Carbon filters. *Adsorbed organics support biological growth on carbon filters*



Experimental evidence

Evidence for the presence of hydrocolloids of high molecular weight in secondary effluents is unfortunately indirect. Busch and Stumm took well-settled activated sludge and centrifuged it at 24,000 G to obtain a supernatant containing the colloid. Presumably, the same substances were present in the supernatant from gravity settling. In my own work, centrifugation at 45,000 G would bring down non-resolvable colloids which were aggregated by freeze-drying. These colloids were effectively removed by clarification with lime or adsorption on a membrane filter.

Other evidence for high molecular weight hydrocolloids in secondary effluents can be deduced from the properties of activated sludge and the slimes on trickling filters. The microorganisms which carry out secondary treatment are flocculated together with a mass of debris and partially assimilated foods such as starch grains. The binding colloid is the capsular material of bacteria aided by hyphae of fungi and filamentous bacteria. Polyhydroxybutyrate polymer has been implicated by Crabtree as a causative agent for floc formation. This sticky, water-insoluble polymer is manufactured in large quantities inside many species of bacteria and appears to cause adhesion between individual cells leading to floc formation. From the earliest studies, the flocs of activated sludge have been described as gels. The properties of activated sludge resemble a well dispersed permanent jelly such as a bacteriological agar that has been broken up in a high-speed kitchen blender. Such a dispersed jelly rapidly clogs ordinary filter paper. Flocs in activated sludge are even more ragged than a chopped up jelly, and offered proportionately greater resistance to filtration.

The quantity of dispersed hydrocolloids present in the effluents from secondary treatment plants is difficult to estimate. Clarification and removal of colloids from a good effluent that is low in turbidity and contains little floc may reduce the total organic carbon (TOC) by as little as 2-4 mg./l. The chemical oxygen demand (COD) of the non-dialyzable material in the soluble fraction of secondary effluents ranges from 5-25 mg./l. The COD of glucuronic acids and related materials can be calculated to be somewhat less than the dry weight.

Natural polymers

The natural polymeric flocculants in waste waters are high molecular weight anionic hydrocolloids very similar in properties to the partially hydrolyzed polyacrylamides and to some natural gums that have already found utility as flocculating agents for waste waters. Busch and Stumm found that the natural polymer which they extracted from activated sludge was effective as a flocculant for silica or dispersed bacteria at concentrations of from 1-10 mg. l. Although most of a polymeric flocculant should be adsorbed at the optimum flocculant dose, activated sludge probably contains an excess of polymer that contributes to its poor dewatering properties. It is characteristic of polymer flocculants that they act

as dispersants when present in an excess over the optimum dose. In many cases, twice the optimum polymer dose will produce complete dispersion.

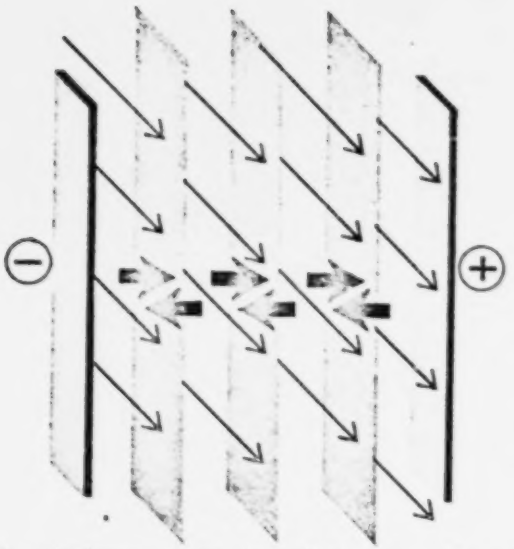
Some natural waters containing algae and other microorganisms have been said to contain proteins or protein-like substances which aid filtration. In other cases, the organic matter in water hinders filtration. Certain surface waters having a fairly low turbidity but high in organic matter are difficult to coagulate and filter unless clay is added as a weighing agent. One function of the clay may be to absorb excess natural polymer which is acting as a dispersing agent.

Clarification of secondary effluents can be achieved by treatment with aluminum or iron salts to form hydrous oxides or by raising the pH with lime or sodium hydroxide. In the latter case, magnesium hydroxide, which precipitates above pH 11, appears to be the effective flocculant. In every case, a well dispersed solid with a large surface area is produced *in situ* where it can absorb polymers from solution. Even though the hydrous colloids are relatively poor adsorbents for small organic molecules, they will adsorb polymeric species as evidenced by the fact that floc properties are altered by the use of such materials. Very little colloidal matter remains in suspension after flocculation with lime. The anionic polymers in secondary effluents also can be neutralized and flocculated by synthetic cationic polymers. Large quantities of the order of 3-5 mg. l. are required which represent a substantial added cost for treatment.

Filtration

Filtration of effluents from biological treatment of waste water is difficult. Slimes derived in part from the natural hydrocolloids accumulate and rapidly clog any surface filter. Better results can be obtained with filtration-in-depth on granular filters. Even here, short filter runs are the rule and frequent vigorous backwashing is necessary to reduce head losses. To get adequate clarity, some form of flocculant such as alum ordinarily is used before a granular filter.

Parkhurst and his coworkers used granular carbon filters to adsorb organic matter from secondary effluent without prior clarification. Frequent backwashing of the first of four 10 foot columns in series was necessary to prevent excessive head loss. Bishop and his associates found that some of the colloidal particles would penetrate six feet of granular carbon and showed that these particles were responsible for the organic matter which penetrated the column. A theoretical analysis indicated that particles at the upper end of the colloidal range would diffuse too slowly to reach the surfaces of the granules in the time the water is traversing the column. Both groups of investigators found that the adsorbed organic matter supported the growth of microorganisms. Some of the removal of organic matter on carbon columns that have been in use for more than a few days can be attributed to biological activity. In this respect, carbon columns closely resemble slow sand filters which must collect a biological slime before they reach full efficiency.



Electrodialysis. *Membrane fouling by colloids eventually reduces salt flux*

Investigators at the Oak Ridge National Laboratory have found that polymeric flocculants and also natural organic colloids can be filtered out on porous membranes to form dynamic ion exchange membranes with hyperfiltration properties that will reject salts. Sulfite pulp mill wastes and humic acids have been used to form membranes with salt rejecting properties that may be useful for reverse osmosis. Work currently under contract to the Federal Water Pollution Control Administration will study the practicality of using this technique to remove organic matter and salts from secondary waste treatment effluents. A potential advantage of this technique is the inherent self-healing properties of dynamically formed membranes.

Other techniques

Electrodialysis is another technique that uses membranes to remove salts from water. Anionic colloids are deposited on the anion permeable membranes which have pores too small to permit their passage. The accumulated colloids eventually reduce the salt flux to unacceptable values. Bacteria growth is also present in the electrodialysis stack. One way to remove colloids is to let the membrane stack rest for a day. During this time, bacteria attack the colloidal matter so that it can be flushed off when the unit is restarted. Some of the colloidal matter that fouls the membrane may be produced by slime bacteria that flourish in this environment.

Distillation of effluents may also be troubled by the presence of polymeric matter in the waste. A thick gummy layer can form on tube surfaces when distilling primary effluents; the organic matter may decompose and produce odors at high temperatures; heat transfer surfaces that operate below temperatures that are lethal to bacteria probably will be fouled by biological growth on adherent slimes.

By way of summary, high molecular weight polymers, which are natural anionic polyelectrolytes bearing an excess of negative charges, are present in the effluents of waste water treatment plants employing biological processes. These colloids are derived principally from the capsular slimes of bacteria and other microorganisms. Although the absolute quantity of polymers is less than 10 mg. l., the effects produced by these hydrocolloids have a large influence on physicochemical processes used to purify waste water. The polymers offer great resistance to filtration and interfere with other membrane processes such as electrodi-

alysis and heat transfer. However, the natural polymers may also form dynamic reverse osmosis membranes with salt-rejecting properties that may be useful in secondary waste treatment.

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